

OST TECHNICAL PROGRESS REPORT TEAM WORK PLAN--FOR FY2001 RESULTS

TITLE: Advanced Separations Technologies Team

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DESCRIPTION: Hydrogen can be produced from natural gas or other fossil feedstocks. However, for hydrogen to be used widely as a transportation fuel, improvements are needed in its production, storage, and use in fuel cells. In FY01, the team conducted research in two major areas: hydrogen separation and advanced hydrogen storage methodologies.

RESEARCH OBJECTIVES: The separations work was conducted in two distinct subtasks. The first was concerned with hydrogen separation and production and focused on the development and testing of hydrogen separation membranes and membrane reactor technology. The second was concerned with advanced carbon research and focused on the fabrication and testing of the novel materials necessary for advanced separation and hydrogen storage technologies

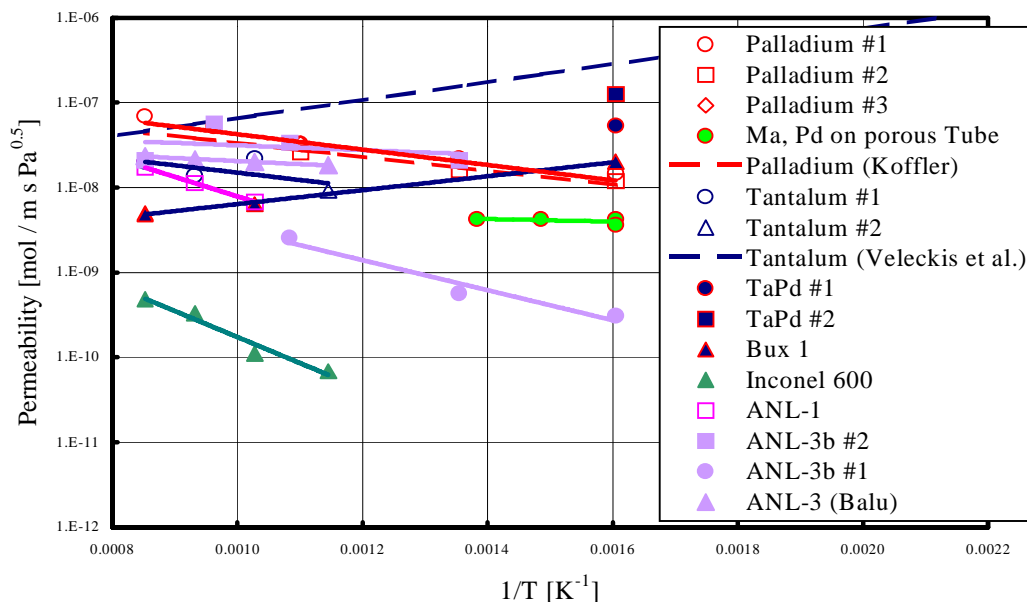
LONG TERM GOALS / RELATIONSHIP TO NETL'S PRODUCT LINE(S): Both the Transportation Fuels and Chemicals and the Advanced Fuels Research Product Plans specifically cite the need for research on advanced hydrogen production and separation technologies. The February 1999 Transportation Fuels and Chemicals Product Plan lists "research to develop high-efficiency hydrogen and synthesis gas production technologies" as part of its multi-year plan (p.36). A work-group product draft report on the July 1999 Industry-Government Workshop on Ultra Clean Fuels for the 21st Century specifically cited "develop improved hydrogen separation /materials technology," both from synthesis gas and other mixed gas streams as an R&D priority (p. 18, 21). The February 1999 Advanced Fuels Research Product Plan lists "high-temperature hydrogen separation technology" as a critical need item (p. 9).

SUMMARY ACCOMPLISHMENTS: Hydrogen Separation -- In FY2001, NETL's Office of Science & Technology performed permeability tests on a total of 20 different hydrogen separation membranes for separating hydrogen from mixed gas streams in its unique high-temperature (900 °C), high-pressure (400 psi) hydrogen membrane test (HMT) unit. This initial set of membranes comprised seven different membrane types from both in-house researchers and external collaborators. They included the bulk metals palladium (Pd), tantalum (Ta), and vanadium (V), Pd-coated Ta membranes from three different sources, a Pd-coated porous stainless steel membrane, and ceramic/metal composites (cermets) from Argonne National Lab. The membranes were tested over a range of temperatures and pressures with a hydrogen/helium gas mixture to determine the suitability of membrane mounting and sealing methods, the hydrogen transport characteristics of the bulk substrate metals, and the baseline hydrogen permeability of the Pd-based membranes. Several membranes demonstrated the ability to provide theoretical hydrogen permeability rates, while surviving for several weeks with tests at even the most severe operating conditions. In addition, work began on the development of membrane reactors to enhance the water-gas shift reaction at high temperature and high pressure without a catalyst. In order to allow for parallel efforts in both membrane separation and membrane reactors, a second HMT unit was constructed.

Hydrogen Storage: Hydrogen storage research focused on the adsorption properties of carbon nanotubes. A tapered element oscillating mass analyzer (TEOM) was used to obtain isotherms for hydrogen adsorption on single-walled carbon nanotubes (SWCNTs) at 25 °C over the range of pressure from one atmosphere to 700 psia. This instrument measures weight changes in a packed bed of adsorbent as a function of hydrogen pressure in a flow-through system. The hydrogen adsorption properties of SWCNTs were investigated as a function of various pretreatments given the samples. In all cases the rates of adsorption and desorption are fast and indicative of physisorption. The isotherms are still ascending at the upper pressure limit of the instrument, and it is clear that the ultimate storage capacity of these materials is not defined by these experiments. The raw and purified SWCNTs samples do not adsorb as much hydrogen as a typical sample of activated carbon under similar conditions. The foremost result is that a simple, controlled oxidation with CO₂ activates SWCNTs for adsorption of hydrogen. A roughly three-fold increase in the amount of hydrogen adsorbed is observed. Adsorption of 1.2 wt% hydrogen was observed at 700 psia in the best case, roughly double that found for the sample of activated carbon. This discovery indicates that the hydrogen storage characteristics of SWCNTs may be significantly improved by manipulation of their physical/chemical structure.

RESULTS:

Hydrogen Separation: The permeability testing mentioned above resulted in the following figure that summarizes some of the results obtained in the HMT unit as a function of temperature.



From our work with bulk tantalum, we learned that it is as sturdy as expected and may be a suitable substrate material for high severity conditions. However, its surface becomes contaminated easily via oxidation or other impurities, which affects its permeability prior to coating. Its hydrogen permeability kinetics are very slow, and we were not able to achieve the permeability that was theoretically expected. This is seen on the above figure when comparing our Tantalum #1 and #2 results with the Tantalum results from Veleckis et al.

We began fabricating our own palladium-coated tantalum membranes and tested them along with those from collaborators such as Robert Buxbaum of REB and James Watkins of the University of Massachusetts. From this we recognized the importance of proper Ta surface preparation and cleaning prior to coating with Pd in order to achieve good permeability and stable membranes. We also were able to achieve permeabilities that were at least as good as those from an external membrane developer, as shown on the figure when comparing our TaPd #1 and #2 data with those of Bux1. However, the Bux1 membrane lasted for 28 days of testing at severe conditions, while the NETL TaPd membranes only lasted for several days. This shows the potential for tantalum to form hydrides or to swell at certain test conditions and hydrogen saturations, which makes it brittle and decreases its durability.

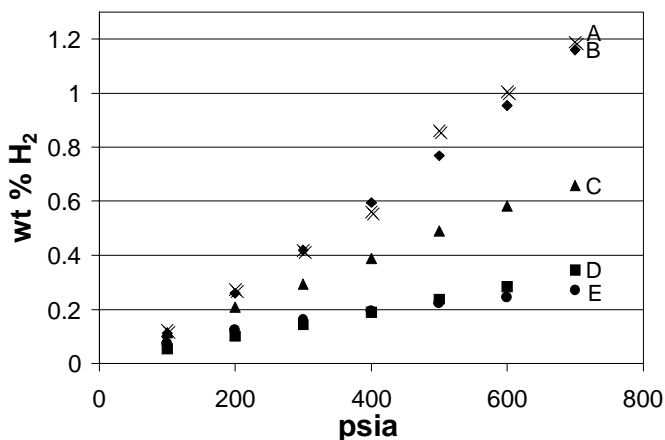
The work on bulk palladium membranes was done at temperatures and pressures that had not been previously reported, yet produced data that was consistent with those in the literature (see our Palladium #1, #2, and #3 data in the figure versus that of Palladium (Koffler)). A much better fit of the data was realized when the hydrogen partial pressure exponent value was optimized to a value of 0.63, as opposed to the conventional 0.50. This result was similar to a previously reported value of 0.68 at 623 K. This deviation of the exponent value from 0.50 to 0.63 for bulk membranes may be attributable to the increased hydrogen concentration in the membrane and/or increased surface resistances with increasing pressure. These tests on bulk Pd were summarized in a draft manuscript that has been submitted to the Journal of Membrane Science, entitled "The Permeability of Hydrogen in Bulk Palladium at Elevated Temperatures and Pressures".

We modified our test unit and conducted our initial test with a membrane with a tubular configuration. The membrane consisted of porous stainless steel coated with palladium from Professor Ed Ma of Worcester Polytechnic Institute. As the data in the figure show (Ma, Pd on porous tube), the results were in good agreement with theoretical values. Because of the thin Pd coating over a porous substrate, they also produced the highest fluxes in our unit to date.

The water-gas shift membrane reactor effort was initiated by determining the kinetics of the reaction at high temperature without a catalyst. The HMT unit was modified in order to run the water-gas shift reaction in either direction. Testing began with the reverse reaction. However, it was quickly discovered that the HMT Inconel reactor itself served as a catalyst, producing extremely high conversions. So an all-quartz reactor was designed, fabricated, and installed. Preliminary tests at the end of the year indicated that this reactor design produced conversions in the expected range.

Finally, a second HMT unit was designed, constructed, and shaken down in order to accelerate the project activities in both hydrogen separation and membrane reactors. It was designed to be more flexible than the first unit in terms of membrane sizes and configurations, gas flow rates, and pressure control.

Hydrogen Storage: Hydrogen isotherms were obtained for several samples of carbon materials as shown in the figure below. A range of adsorption capacities was found depending on the source of carbon and the pretreatment given before the isotherm was taken. An activated carbon was included for comparison to the carbon nanotube samples. As may be seen, some nanotube samples are inferior to the activated carbon, but others are clearly superior.



Comparison of Adsorption Isotherms of Hydrogen on Various Carbons. A. CO₂ Oxidized “Raw Material” Rice SWCNT. B. CO₂ Oxidized Purified Rice. C. Activated Carbon. D. Purified Rice SWCNT after Pyrolysis at 700°C. E. “Raw Material” Rice SWCNT.

The nanotubes used in this work were supplied by Tubes @ Rice. The synthesis was by the laser ablation method using a Ni/Co catalyst. “Raw” tubes are supplied as recovered from the synthesis. “Purified” tubes are derived from the “Raw” material by oxidation in refluxing 2.6 M HNO₃ for 12 hours. All of the samples contain oxygen as a result of oxidation received either on exposure to air

or in a greater degree by the purification technique. In some cases, pyrolysis of the sample was carried out by heating in the TEOM reactor to 700 °C before the isotherm was taken. The loss of carbon oxides was apparent on heating by observation of both a decrease in sample weight and detection of the oxides by a down-stream mass spectrometer. The effect of pyrolysis on the isotherms was measurable, but relatively small.

A significant improvement in the adsorption characteristics of both purified and raw nanotubes was obtained through a simple activation technique. The procedure was to expose the sample to a stream of CO₂ in a tube furnace heated to 600 °C. This caused a weight loss of 14 % of the “Raw” material and 37% of the Purified material. A detailed study of the nanotubes before and after oxidation under CO₂ was carried out using TGA and CAPTO. The results of these analyses show that CO₂ oxidation selectively removes the most reactive carbon species in the samples. Taking the differential of the TGA curves shows that the complex pattern found for the purified nanotube sample was reduced to a simple one containing mainly one peak after activation. For both the Raw and Purified samples, the remaining material demonstrated hydrogen storage that was increased by a factor of about three, reaching 1.1 – 1.2 wt% at 700 psia. The upper limit of pressure for the isotherms shown in the Figure is dictated by the pressure limit of the instrument. The ultimate amount of hydrogen that could be adsorbed at higher pressures is obviously much greater than reported here, but has not yet been established. The results indicate that the gas adsorption properties of nanotubes can be manipulated by both chemical and physical means and that it is reasonable to expect further improvements can be obtained.

PUBLICATIONS/PRESENTATIONS:

Publications:

Rothenberger, K., Morreale, B., Enick, R., Ciocco, M., Howard, B., Cugini, A., and Morsi, B. (submitted). Permeability of palladium at elevated temperature and pressure. Journal of Membrane Science.

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Presentations:

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ACKNOWLEDGMENTS: The project was sponsored by the FE Transportation Fuels and Chemicals Product Line and the FE Advanced Fuels Research Product Line. NETL's site support contractor for OST, Parsons Infrastructure & Technology, performed the hydrogen separation work. For additional information about this project, contact Brad Bockrath.